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Direct evidence for coastal iodine particles from *Laminaria* macroalgae – linkage to emissions of molecular iodine

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Abstract

Renewal of ultrafine aerosols in the marine boundary layer may lead to repopulation of the marine distribution and ultimately determine the concentration of cloud condensation nuclei (CCN). Thus the formation of nanometre-scale particles can lead to enhanced scattering of incoming radiation and a net cooling of the atmosphere. The recent demonstration of the chamber formation of new particles from the photolytic production of condensable iodine-containing compounds from diiodomethane (CH_2I_2), (O'Dowd et al., 2002; Kolb, 2002; Jimenez et al., 2003a; Burkholder and Ravishankara, 2003), provides an additional mechanism to the gas-to-particle conversion of sulphuric acid formed in the photo-oxidation of dimethylsulphide for marine aerosol repopulation. CH_2I_2 is emitted from seaweeds (Carpenter et al., 1999, 2000) and has been suggested as an initiator of particle formation. We demonstrate here for the first time that ultrafine iodine-containing particles are produced by intertidal macroalgae exposed to ambient levels of ozone. The particle composition is very similar both to those formed in the chamber photo-oxidation of diiodomethane and in the oxidation of molecular iodine by ozone. The particles formed in all three systems are similarly aspherical and behave alike when exposed to increased humidity environments. Direct coastal boundary layer observations of molecular iodine, ultrafine particle production and iodocarbons are reported. Using a newly measured molecular iodine photolysis rate, it is shown that, if atomic iodine is involved in the observed particle bursts, it is of the order of at least 1000 times more likely to result from molecular iodine photolysis than diiodomethane photolysis. A hypothesis for molecular iodine release from intertidal macroalgae is presented and the potential importance of macroalgal iodine particles in their contribution to CCN and global radiative forcing are discussed.

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1. Introduction

Following extensive studies into coastal aerosol formation (O'Dowd et al., 1999, 2002) and recent insights into the production of iodine-containing particles from chamber studies of the photo-oxidation of diiodomethane (O'Dowd et al., 2002; Kolb, 2002; Jimenez et al., 2003a; Burkholder and Ravishankara, 2003), it has been proposed that the atmospheric oxidation of macroalgal iodocarbon emissions yield condensable iodine vapours and form the observed new particles. Incubation studies of kelps at Mace Head Atmospheric Research Laboratory (53°19' N, 9°54' W), the site of many of the ultrafine particle measurement campaigns, have already shown that CH₂I₂ is the dominant organic iodine species released from the common rocky shore algae *Laminaria digitata* and *Laminaria saccharina*. CH₂I₂ readily photolyses to yield iodine atoms at ambient light levels. The subsequent reactions of iodine have been widely studied and used in investigations of marine boundary layer halogen cycling (McFiggans et al., 2000). The iodine monoxide radical (IO) is formed by reaction of iodine atoms with ozone and establishes a rapid steady state with iodine atoms owing to its rapid photolysis. Condensable iodine species are produced by the IO self-reaction and by the reaction of IO with the hydroperoxy radical (HO₂) or nitrogen dioxide (NO₂). The products of these reactions have been proposed to condense on pre-existing supercritical embryos (so-called thermodynamically stable clusters, TSCs) leading to sufficiently rapid growth to significantly increase their lifetime with respect to coagulation. This stabilisation thereby increases their probability of growing to sizes where they can act as CCN. The TSCs are assumed to be supercritical in their nucleation mechanism, conceptually downstream of the saddle-point on their free energy surface and so more likely to grow in their nucleating vapours than evaporate. It has been postulated (Pirjola et al., 2000) that significant numbers of TSCs may exist in the clean marine boundary layer in the homogeneous nucleation of H₂SO₄-H₂O-NH₃. However, it has been established that ambient ammonia and sulphuric acid were unable to explain condensational growth to observable sizes and that additional species were required (O'Dowd et al., 1999).

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Indirect in situ measurements have indicated that ultrafine particles are not sulphate dominated and may indeed contain iodine (Mäkelä et al., 2002). It has been hypothesised therefore that gaseous iodine compounds formed in the photo-oxidation of CH₂I₂ emitted from coastal macroalgae, condense onto ammonium sulphate clusters leading to an enhanced number of CCN in the marine boundary layer. However, it was discovered as long ago as 1928 (Dangeard, 1928; Kylin, 1929) that natural release of “free” iodine (I₂) from kelps, a process known as “iodovolatilisation”, occurred leading to the higher iodine content of air in coastal areas (Dangeard, 1957). Consistent with this, very recent observations of molecular iodine (I₂) in the coastal boundary layer (Saiz-Lopez and Plane, 2003) at Mace Head indicate that I₂, rather than iodocarbons, may be the dominant source of coastal reactive iodine. This study investigates the formation of iodine-containing particles from kelps and discusses mechanisms for coastal I₂ and particle production.

2. Method and Results

2.1. Laboratory investigation of particle production on exposure of *Laminaria* macroalgae to ozone

To investigate the coastal formation of new iodine-containing particles from intertidal macroalgae, we conducted a series of flow reactor experiments, exposing *Laminaria digitata* macroalgal samples cropped from intertidal rock pools to a flow of moderately ozonised air. *Laminaria digitata* specimens were cropped from the infralittoral zone at the Mace Head site. The specimens were immediately placed in a 10 L reactor vessel and exposed to an ozonised stream of charcoal scrubbed, particle-free air under ambient light conditions and in the dark. The exhaust from the reactor was sampled using a TSI model 3081 scanning mobility particle sizer (SMPS), a TSI model 3025 condensation particle counter and an Aerodyne aerosol mass spectrometer (AMS) (Jayne et al., 2000; Allan et al., 2003). The SMPS was used in two ways; i) scanning the volt-

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age on the central rod to measure the full distribution and ii) maintaining a series of constant voltages to deliver a range of monodisperse aerosol to the AMS. The AMS was used to measure full mass spectra of both the polydisperse distribution and the monodisperse size cuts and to build aerosol time-of-flight mass distributions of individual m/z fragments (Jimenez et al., 2003b). Two additional series of experiments were carried out. The first on samples of *Laminaria hyperborea* (Gunnerus) Foslie, also widespread around the Mace Head coastline, cropped from the Menai Straits between the North Wales mainland and the Island of Anglesey (53°13' N, 4°11' W) and the second on samples of *L. digitata* (Huds.) Lamour (and also on *L. saccharina* (L.) Lamour) sampled near the Scottish Association for Marine Science laboratory at Dunstaffnage, near Oban, Scotland (56°27' N, 5°26' W). In the latter experiments, the samples were cropped intact and were kept at 3°C in cold room tanks exposed to a typical day/night light cycle. The seawater was frequently replenished with filtered seawater from the location where they were cropped. These latter two series of experiments allowed variation in the geometry of the experimental setup ensuring elimination of potential artefacts in the original experiments, but otherwise provided data entirely consistent with the experiments conducted in situ at Mace Head. In addition an ozone analyser (Monitor Labs ML8810) and a more directly adjustable ozone generator (PenRay model SOG-2) were used to more accurately control and measure the ozone concentration. Together, these experiments provide the first direct evidence for ultrafine particle production from coastal macroalgae under atmospheric and close to atmospheric conditions. Figure 1 shows a schematic of the experimental apparatus. Size distribution measurements showed that the numbers and sizes of particles formed were extremely repeatable with the total aerosol number and volume increasing with increased ozone concentration. Figure 2 shows the average of 7 distributions taken with different specimens over three days during the Mace Head measurements at the same elevated ozone concentration (of the order of 300 ppbv); the error bars indicate the extent of the macroalgal specimen-to-specimen variability.

Total flow rates in the experiments were largely determined by the required flow rates

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for the sampling instrumentation but ranged from 0.4 to 2.5 L min⁻¹. The flows in the zero air and ozonised air lines were independently controlled, but in all cases pre-scrubbed through charcoal and filtered for particles. Both flows were bubbled through water; the ozone line to scrub hydroxyl radicals and the air line to maintain a humid flow to ensure that the *Laminaria* did not dry out. A range of ozone mixing ratios from zero to around 300 parts per billion (ppbv) was used for the experiments. Table 1 is a “truth table” summarising the system response to experimental conditions. It can be seen that no particles were formed in the absence of either light or ozone. It was initially found that no particles were formed unless ozonised air passed directly over the sample, i.e. post-mixing of even elevated ozone concentrations with ozone-free air that has passed over the seaweed will not lead to particle formation within the residence time between the post flow reactor ozone inlet and the sampling instruments. However, addition of a secondary reaction vessel, which increased the post-exposure residence time, led to significant particle detection whether the ozonised air was introduced prior to, or after, the primary reactor. This suggests that any particles formed from precursors released by the seaweed do not have time to grow to a size which can be detected by the particle counter when the ozone was introduced after the seaweed reactor under the original experimental configuration, i.e. they remain significantly smaller than 3 nm in the shorter residence time corresponding to the tubing between the primary reactor and particle detectors. However, the increased (several minutes) residence time corresponding to the secondary reactor is comparable to or greater than the transit time across the intertidal zone at Mace Head. It is proposed that in both the laboratory experiment and the open coastal atmosphere, the transit time plays an important role in the growth of particles to a size detectable by instrumentation. Indeed, in general it was found that, as the characteristic residence time in the system decreased (by increasing the gas flow rate), the threshold ozone concentration required to form detectable particles increased. This is not unexpected, since the smaller the residence time the greater required rate of condensable vapour production to form particles of detectable size.

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Importantly, it must be recognised that these experiments involve living biological systems and the factors controlling the *Laminaria* iodine metabolism are not entirely understood. Active control of these factors was therefore not attempted other than to ensure measurable experimental conditions including flow rates, gas concentrations, humidity and either light or dark. The resulting behaviour in terms of, for example, absolute particle concentrations formed or representative ozone concentrations for particle detection varied between experiments but followed the trends described above and presented in Table 1. It was noted that multiple exposures of individual plants to the same ozone concentration produced continually reducing numbers of particles. It was also noted that the plants “recovered” with time, such that re-exposure to the original ozone concentration led to increased numbers again. The absolute magnitude of the decline and the time required to recover were again variable and depended on the exposure time, the number of exposures and varied between plants. The results presented are those from fresh or fully recovered specimens. It was noted that the light levels led to significant variability as might be expected. The results presented simply contrast the system behaviour when exposed to daylight and when blacked out by a darkroom curtain – no control of light level was used in these experiments due to the configuration. Additional contributions to the variability may have been due to the increasing age of the specimens since being cropped throughout the experimental programme. The experiments were carried out over several months, however no qualitative and little quantitative difference was found using the same conditions at the beginning and end of the programme.

Increasing the ozone concentration further (to around 500 ppbv) with the increased residence time, it was possible to grow the aerosol to sizes significantly greater than the lower size cut-off of the AMS, limited by the configuration of the aerodynamic lens inlet. Zhang et al. (2002) have used computational fluid dynamic calculations to describe the transmission through a single orifice and have expanded this to model the aerodynamic lens system used in this study showing that it has a lower size cut off of 30 nm. Figure 3 shows a typical mass spectrum of particles formed in the exposure of

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L. digitata to ozone. It can be seen that all the major mass fragments are consistent with being derived from iodine oxides or iodine-containing oxyacids, as they were in the chamber study of the photolysis of CH_2I_2 (O'Dowd et al., 2002; Jimenez et al., 2003a) and that the same fragments are present (I^+ , HI^+ , IO^+ , HIO^+ , IO_2^+ , HIO_3^+ , I_2^+ and I_2O^+).

5 Although the plot in the figure does not show fragments below m/z 100, the m/z fragments corresponding to sulphate (SO^+ , SO_2^+ , SO_4^+ at 48, 64 and 96, respectively) and nitrate (NO^+ and NO_2^+ at 30 and 46) were absent indicating that there was little mass contribution in the aerosol from either species. Although this cannot entirely eliminate the participation of sulphur or nitrogen containing species in the particle formation process, the scrubbing and filtration of the flowstream should have minimised the influx of condensable material into the system.

10 By positioning the SMPS upstream of the inlet, it was possible to introduce monodisperse size cuts into the AMS. Building mass distributions of selected iodine mass fragments as a function of vacuum (more correctly “free molecular”) aerodynamic diameter, it was then possible to estimate the effective density of the particles by equating the modal aerodynamic diameter to the mobility diameter of the monodisperse cut. Figure 4a shows the mass distribution of the I^+ and I_2^+ fragments (m/z fragments 127 and 254) in 120 nm mobility diameter particles. Figure 4b shows plots of the aerodynamic mode diameter of these fragments for a range of mobility diameters. The slope of the plots shows that the effective density, a measure of the material density and the shape of the particles is of the order of 3.5 g cm^{-3} . This is lower than the density of higher oxides of iodine such as I_2O_5 (4.78 g cm^{-3}), indicating particle asphericity if they are made of such materials. For details of this analysis, the reader is referred to Jimenez et al. (2003a).

25 **b) Particle formation in the reaction of molecular iodine with ozone**

A sequence of experiments was conducted to investigate the formation of particles in the light and dark reactions of molecular iodine with ozone. The experimental apparatus was slightly modified to pass air across the headspace of a small trap containing crystalline iodine at a known temperature, thus controlling the molecular iodine

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vapour pressure. Again, particles formed mixing this airstream with ozonised air were sampled with a variety of instrumentation, and again extremely high and repeatable particle number concentrations were observed throughout a range of ozone and iodine concentrations. The particle composition was found to be very similar in these and the seaweed exposure experiments to those formed in the chamber photo-oxidation of CH_2I_2 ; consistent with the particles comprising almost exclusively iodine oxides and oxy-acids. Figure 5 shows the mass spectra from each of the three systems – it is evident from the relative fragment intensity that the particles formed in all systems have extremely similar composition. In the exposure of molecular iodine to ozone, particles were formed both in the presence and absence of light, contrary to atmospheric observations, the seaweed experiments and the findings of the chamber study. However, particle formation in the dark was less intense than at ambient light levels, requiring extremely high ozone and iodine concentrations; much higher than may be expected in the atmosphere. Reducing the iodine and ozone concentration towards ambient levels, particle production in the dark became undetectable.

The seaweed experiments were all conducted under humid conditions with moist *Laminaria* specimens. The molecular iodine experiments were conducted under both dry and moist conditions. In all experiments, the particles were significantly more compact and dense than those formed in the CH_2I_2 chamber photo-oxidation. Those formed under dry conditions in the chamber study possessed distinct fractal morphology. This was not so evident for the particles formed in the current study. Particles were captured on holey carbon film coated copper mesh grids (Agar Scientific). Transmission Emission Microscope (TEM) imaging and analysis was carried out using a JOEL 2000EX instrument, operating at 200 kV, with associated X-ray microanalyser. The X-ray analysis will not be presented here, as this is the subject of further studies. Figure 6 shows a TEM image of a particle formed in the light reaction of molecular iodine and ozone; those formed in the seaweed experiments are equally compact. It appears that the particles formed in the reaction of molecular iodine with ozone do not clearly exhibit the degree of fractal morphology inferred from the CH_2I_2 chamber experiments,

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possessing a more compact agglomerate form consistent with the effective density of those formed passing ozone over *Laminaria* macroalgae. This may be more due to the differences between the formation conditions in the flow and chamber experimental configuration than in the chemistry and it is not possible to positively identify the participating species from these particle morphology differences.

In order to investigate the behaviour of the particles when exposed to water vapour, a hygroscopicity tandem differential mobility analyser (HTDMA) was used (Rader and McMurray, 1986). This instrument relies on measuring the change in a particle's size by monitoring the change in its electrical mobility on increasing the humidity of its environment. In the HTDMA, a Vienna-type differential mobility analyser (DMA) (Winklmayr et al., 1991) selects a near-monodisperse distribution of dry particles ($< 10\%$ RH) from the polydisperse distribution sampled from the reactor output. The monodisperse size cut of particles is then exposed to a controlled humidity environment before being passed into the second DMA. Rapid and accurate humidity control is achieved through mixing of dry and saturated airflows using computer controlled variable flow pumps. Particles taking up water normally exhibit growth in the humid environment – the second DMA is scanned over an appropriate size range and the size-selected particles are counted using a condensation particle counter (CPC) (TSI model 3760). A plot of size from the second DMA versus CPC particle count will then give a distribution determined by the change in size of the original monodisperse population and a broadening effect due to the instrument transfer function. In order to remove this broadening effect of the two DMAs, a modified optimal estimation method (OEM) after Rodgers (2000) was used, ensuring that the reported distribution reflected only the particles' change in size (this procedure is the subject of a detailed Technical Note, Cubison et al., personal communication). Figure 7 shows dry to 90% RH growth factor (GF_D) distributions measuring the particles produced in both the light and dark reactions of I_2 with O_3 . It can be seen that very similar trends apply. Rather than growing due to an increase in the bound water content of soluble material in the particles with increasing humidity, the particles appear to be less hygroscopic the larger the dry size. This trend is consistent

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across all sizes in the dark reaction (almost no particles were formed larger than 35 nm diameter in the dark reaction, even with extremely elevated I_2 and O_3 levels). In the light reaction, growth factor distributions were statistically indistinguishable at the lower sizes from those of the particles formed in the dark reaction. At larger sizes (mobility diameter 60 nm), beyond the largest formed in the dark reaction, the particles actually shrank significantly in the more humid environment. The implication is that the particles collapse more completely due to capillarity forces when they are larger, indicating that they become less compact with increasing size. This reflects the mode of growth of the particles. In contrast to the findings from the chamber studies of Jimenez et al. (2003), this trend was the same whether the particles were initially formed in a dry or a humid environment. However, it is not known whether the hygroscopic behaviour of particles formed in the I_2 experiment in a flow reactor or in the CH_2I_2 chamber experiments was closer to that of those formed by *Laminaria* in coastal airmasses.

In all experiments, particle-free scrubbed air was used in both the air and ozone lines. Gaseous H_2SO_4 was expected to be below the threshold required for nucleation. It can be concluded that iodine species alone are responsible for both the nucleation and condensational growth of particles in the experiments. This is borne out by the absence of any significant mass of non-iodine fragments in the mass spectra of particles grown up to detectable sizes (higher than ambient ozone concentrations). Certainly, in the seaweed system, no mass spectrometric signal characteristic of any sulphate fragment was detected above the instrumental noise indicating that there is no significant amount of sulphate mass. Whilst it cannot be categorically stated that there is no sulphate nucleus upon which the iodine species condense, it may be considered unlikely. Since large numbers of particles are formed at ambient ozone concentrations (too small to have their composition probed but large enough to be detected and sized), there is no reason to suspect that a thermodynamically stable sulphate cluster is required for nucleation to occur. It only remains to ascertain whether the condensation of iodine containing vapours on such clusters competes with homogeneous iodine oxide nucleation in the open atmosphere.

3. Daytime observations of molecular iodine in the marine boundary layer

As discussed above and as shown in Fig. 5, it is not possible to unambiguously attribute the formation of new particles to a particular precursor solely based on discrepancies between the properties of particles formed in the laboratory ozonolysis experiments. Suspecting that there was a possible inorganic source of iodine atoms playing a role both in cycling of reactive halogens and in the production of particles, it was decided to search for a variety of iodine-containing species using differential optical absorption spectroscopy (DOAS). During the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) at Mace Head the long-path DOAS instrument was used to measure ambient concentrations of gaseous molecular iodine. The instrument consists of a Newtonian telescope and a 0.5 m Czerny-Turner spectrometer coupled to a two-dimensional charge coupled detector. The transmitting Newtonian telescope was located in a cottage on the shoreline at Mace Head and the light beam was folded back to the transmitter by a retro-reflector situated 4.2 km away on Croaghnekeela Island, providing an effective optical path of 8.4 km over the sea surface. The spectral region between 535–575 nm was utilised for spectra analysis of I₂ with a resolution of 0.25 nm. An additional set of spectra was recorded to cancel out interferences caused by atmospheric scattered light and spectral features of the Xenon lamp. Spectra were accumulated for 30 min for each reported I₂ measurement. During de-convolution each spectra passed through a Fast Fourier Transform (FFT) routine with high and low pass filters. The concentrations were then derived using a least squares singular value decomposition routine comparing the atmospheric spectra with a set of reference spectra. The molecular iodine reference spectrum was obtained from the corresponding cross-section measured in the laboratory (Saiz-Lopez et al., 2004) adapted to the instrument function of the DOAS spectrometer.

Owing to the extensive range of species being investigated across a broad range of wavelengths with different diurnal patterns, the I₂ absorption region was not continuously monitored. Instead, the regions of interest were stepped through sequentially.

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An extensive dataset of molecular iodine spectra were taken over a period of a month (Saiz-Lopez and Plane, 2003). However, most of these were at night. Since particle bursts are almost exclusively observed during the daytime, the most relevant measurements are obtained from the daytime spectra. Figure 8 shows the measurements from each of the three daytimes when spectra were recorded in the I_2 wavelength region. It can be seen that on two of the days, 25 and 26 August 2002, the levels of I_2 were frequently above the detection limit, reaching peak mixing ratios in excess of 25 parts per trillion (ppt).

In order to find out whether these levels produce significant iodine atom fluxes, it is necessary to calculate their rate of dissociation under daytime marine boundary layer conditions.

4. Determination of the photolysis rate of molecular iodine and coastal zone iodine atom flux

The photolysis rate of molecular iodine was directly determined in the laboratory by an optical absorption technique (Saiz-Lopez et al., 2004) in order to confirm the rates calculated from the absorption cross-section, measured or modelled actinic flux and reported quantum yield. With the light intensity at one solar constant in these experiments, the observed first-order destruction rate of I_2 , corresponding to its photolysis, was 0.14 s^{-1} . In this same study, a newly measured high resolution I_2 absorption cross-section from $\lambda = 182$ to 750 nm was reported. This is in good agreement with the more coarsely resolved measurement of Tellinghuisen (1973). Using a two-stream radiative transfer model (see McFiggans et al., 2000), previously reported values of unity for the I_2 quantum yield (Rabinowitch and Wood, 1936) and the new absorption cross-section, a midday, mid-latitude, midsummer photolysis rate yielding 2 iodine atoms was calculated to be in very good agreement at 0.15 s^{-1} .

Diiodomethane has previously been identified as the measured iodocarbon providing the greatest iodine atom flux. Using the DOAS measured I_2 , measurements of

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CH₂I₂ made at ~20 m asl, approximately 50 m from the high tide mark using a Perkin Elmer Turbomass GC-MS (Wevill and Carpenter, 2003) and wavelength resolved surface actinic flux levels measured by spectral radiometry (Edwards and Monks, 2003) it is possible to directly compare the iodine atom flux at Mace Head whenever there was overlap from the measurements. Figure 9 shows such a comparison (note that only where the time series were continuous were measurements available). It can be seen that there was at least three orders of magnitude greater atomic iodine flux from the photolysis of the available molecular iodine than from the photolysis of CH₂I₂; on many occasions this difference was much greater. It should be noted that this comparison assumes that the DOAS measured I₂ is well mixed along the instrument's light path and that CH₂I₂ is well mixed up to the sampling inlet at 20 m. If the I₂ source is solely in the intertidal zone, a maximum of only a few hundred metres of the path, the calculated atomic iodine flux from molecular iodine could be a further factor of 20 to 50 times greater (though this may be partially offset by iodocarbons being more concentrated in the lowest few metres rather than mixed up to the sampling height). Since the GC/MS measured in selective ion mode, it is possible that other organic iodine compounds are present which may significantly contribute to the iodine atom flux. However, although both iodoform (CHI₃) and iododibromomethane (CHIBr₂) have been identified in seawater around incubated seaweeds, no species more photolabile than CH₂I₂ have been isolated in the atmosphere. It is likely therefore that any particles comprising mainly iodine oxides are derived from molecular iodine, not organic iodine.

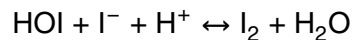
5. A hypothesised mechanism for coastal new particle production

Laminaria species accumulate iodine to levels up to 30 000 times more concentrated than seawater (Küpper et al., 1998). They exchange the iodine with the seawater depending on the oxidising environment of the plant. The reader is referred to Küpper et al. (1998), for a discussion of the factors affecting this transfer. Once the iodine species have diffused across the cell membrane into the apoplast, they are in free diffusive con-

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tact with the surrounding seawater. The studies of Dangeard (1928) and Kylin (1929) showed that iodovolatilisation took place in the apoplast and required oxygen. More recently it has been shown (Küpper et al., 1998) that the oxidation of iodide (I^-) by hydrogen peroxide in the apoplast leads to the formation of hypoiodous acid (HOI). It is known that HOI and I^- establish an equilibrium with molecular iodine in aqueous solution (Truesdale, 1995):



As the water recedes, the kelp beds are uncovered such that at low tide, complete plants may be exposed, covered only with a film of water. The plants will also be exposed to the oxidising atmosphere. The oxidative formation of HOI in the apoplast will lead to a strong iodine solution in free diffusion with the thin water film. This will lead to displacement of the equilibrium towards molecular iodine. Being of limited solubility and relatively volatile, the molecular iodine will then equilibrate between aqueous solution and the gas phase. An additional contribution to the I_2 release is that the oxidative stress on the seaweed during low tide atmospheric exposure may lead to direct I_2 formation on oxidation of I^- by H_2O_2 (Luther et al., 1993). This may lead directly to atmospheric emission. The crucial requirement is that I_2 volatilises before it can react with organic material in the seawater. Whichever mechanism is responsible for forming the I_2 , it is postulated that low tide enables it to escape from the water film before it has a chance to react with organic material. This cannot happen at higher water. Either mechanism for I_2 release is consistent with this study, and resolution of this question is beyond the scope of this study. On the basis of the evidence presented here, it is suggested that the molecular iodine released into the atmosphere in this way photolyses to provide the majority of the available iodine atoms that react with atmospheric ozone leading to the formation of iodine monoxide. The self-reaction of iodine monoxide leads to the formation of higher oxides, the subsequent polymerisation of which lead to clusters, growing by further condensation to form the iodine containing particles. Burkholder et al. (2003) have explored a subset of this mechanism (the clustering of OIO only) in their study of the photolysis of CF_3I and CH_2I_2 and find that published

IO and OIO is incapable of explaining the observed particle bursts. A more extensive clustering mechanism based on an extension of the current work is the subject of ongoing laboratory and modelling studies.

6. Comment on possible effect on climate change

5 Considered alongside the results from the chamber study, it is unlikely that particles observed in the coastal boundary layer are formed from diiodomethane photo-oxidation, given the relative iodine atom flux from molecular iodine. More importantly, intense particle formation does not appear to rely on iodine-containing compounds condensing on sulphate TSCs under ambient conditions. Since this is the mechanism that has been
10 proposed for TSC stabilisation, it is not clear that macroalgal iodine particles will significantly contribute to cloud condensation nuclei or affect global radiative forcing in this way. In order to investigate whether there is such a contribution to CCN number, the exact formation route for the “iodine-only” particles must be established. In particular the role of inorganic iodine compounds, specifically molecular iodine, must be investi-
15 gated. Although iodine species may not be involved in stabilisation of TSCs, particles comprising only iodine species may directly lead to CCN formation. This mechanism must then be investigated in competition with condensational growth of iodine compounds onto TSCs to establish whether it is possible for iodine chemistry to lead to an enhanced number of particles crossing the coagulation barrier and hence to assess
20 the effect on CCN population and radiative forcing.

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Table 1. Truth table showing the system response to ozone introduction position and light conditions. The ozone mixing ratios are representative values for the experiments. In many cases particle production was observed at very much lower mixing ratios (a few tens of ppb), though this was not always repeatable, being dependent on the number of previous exposures, light levels etc. The light levels were not controlled in these experiments and depended solely on the ambient insolation.

Seaweed	1°			2°			Particles
	O ₃	ppb	hv	O ₃	ppb	hv	
✓	✓	100	✓				✓
✓	✓	100	✓			✓	✓
✓			✓	✓	200	✓	✓
✓			✓	✓	100		x
✓	✓	100				✓	✓
✓				✓	100	✓	✓
✓			✓			✓	x
✓	✓	> 500					x
Seawater only	✓	> 500	✓				x

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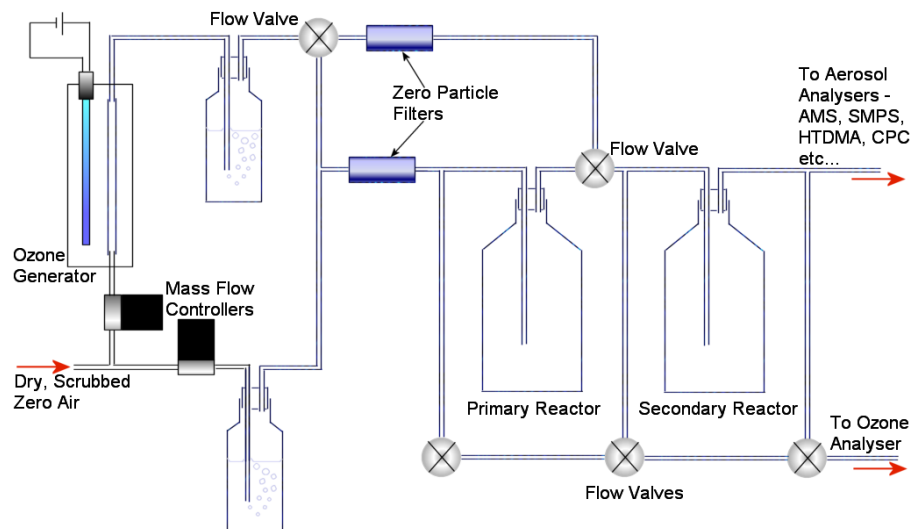


Fig. 1. Schematic of the laboratory apparatus. Dry, scrubbed air was bubbled through double deionised water and any particles were filtered out before passing through the primary reactor containing the *Laminaria* sample. Ozonised air was bubbled through double deionised water to remove free radicals and likewise scrubbed of particles prior to introduction either before or after the primary reactor. The reactors were kept in the dark or exposed to ambient light levels. All joints were glass or stainless steel. The exhaust from the primary reactor was passed into a secondary vessel to increase the reaction time before analysis of the particles formed.

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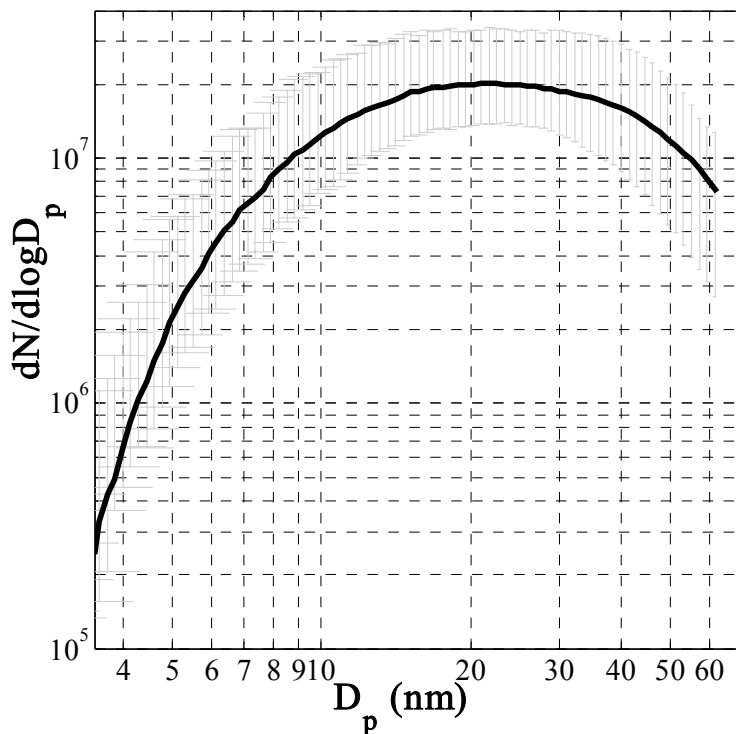


Fig. 2. The average of seven aerosol mobility size distributions measured by the SMPS over several days with four *Laminaria* samples exposed to the same elevated ozone level (around 300 ppb) and illuminated by ambient daylight at Mace Head. The bars show the maximum and minimum concentrations at each size. It can be seen that the distributions are extremely repeatable under these conditions.

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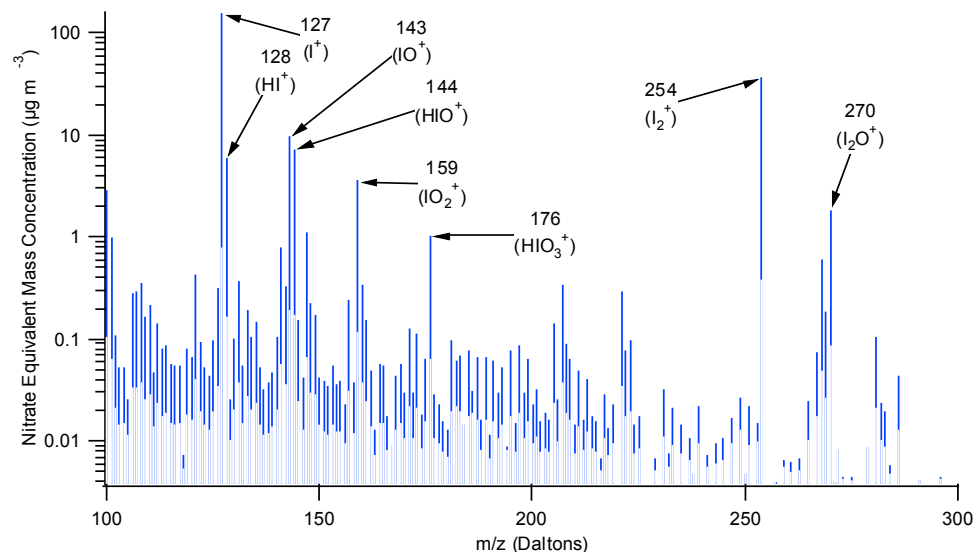
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Fig. 3. A typical positive ion mass spectrum taken with the AMS of particles formed from the exposure of *Laminaria digitata* to 500 ppb of ozone at Mace Head. The major iodine fragments are identified. All the major mass fragments are consistent with being derived from iodine oxides or iodine-containing oxyacids.

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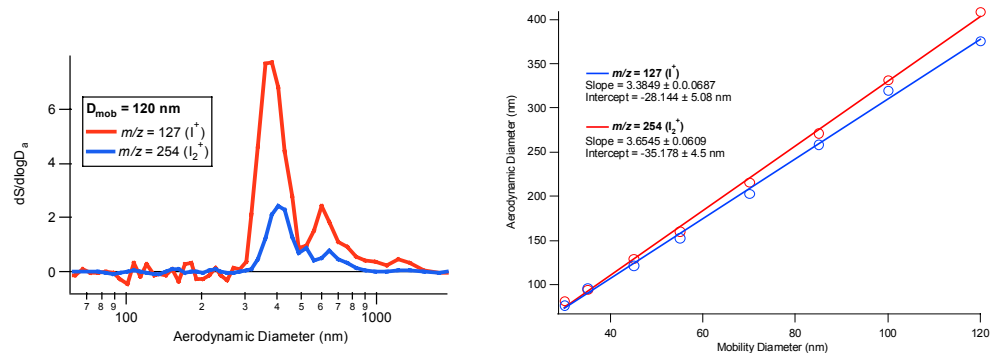


Fig. 4. (a) The aerodynamic size distribution of mass fragments at $m/z = 127$ and 128 corresponding to I_1^+ and I_2^+ for a mobility size cut at 120 nm. Derived from a range of these mass distributions selected at different mobilities, (b) shows the aerodynamic mode diameter plotted against the mobility diameter. The slope of the plot gives the effective density. See text and Jimenez et al. (2003a).

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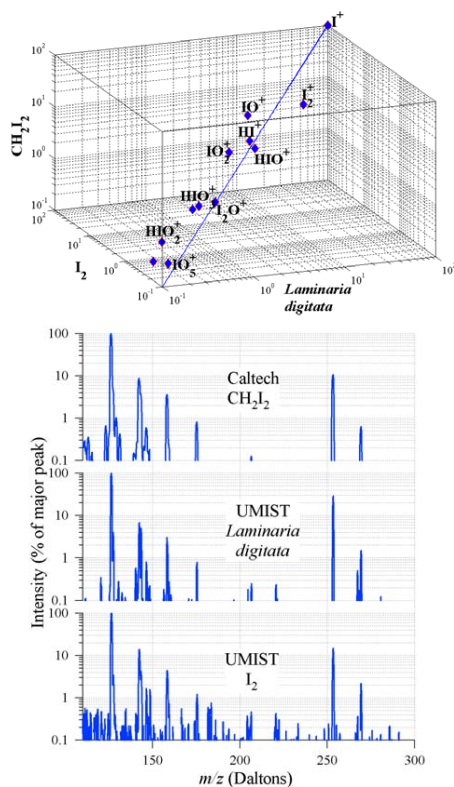


Fig. 5. Mass spectra from each of the three systems i) CH_2I_2 exposed to ozone in the study reported in O’Dowd et al. (2002) and Jimenez et al. (2003a), ii) *Laminaria digitata* and iii) iodine vapour exposed to ozone, this study. It can be seen that the mass spectra of the particles formed in each system are extremely similar. A scatter plot of the major mass fragments in each system is shown in the top panel. It may be inferred that the particles have the same composition in each case.

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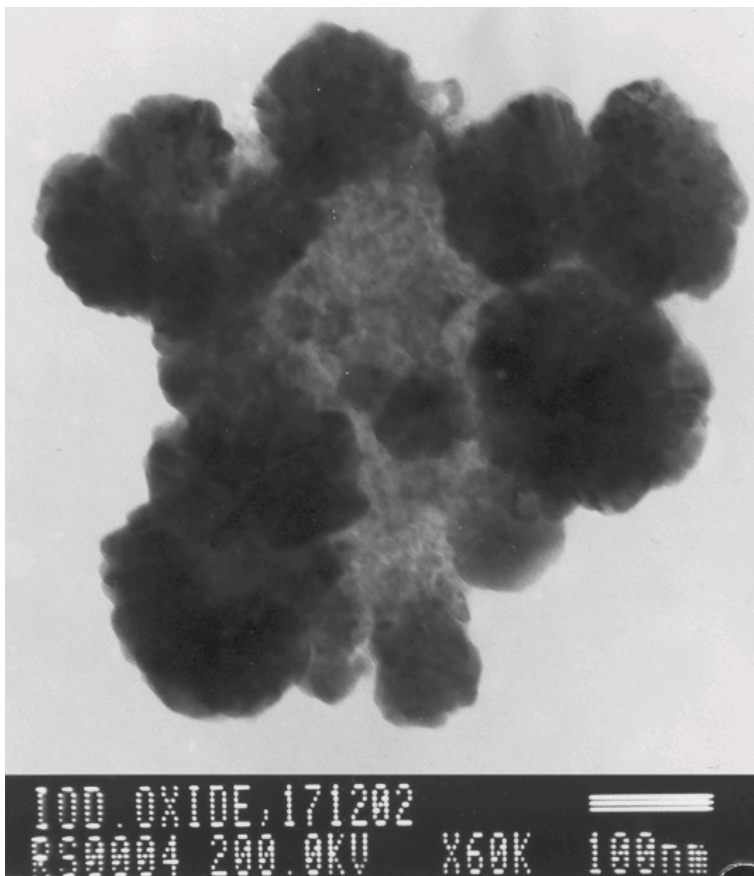


Fig. 6. TEM image of a particle formed in the light reaction of molecular iodine and ozone.

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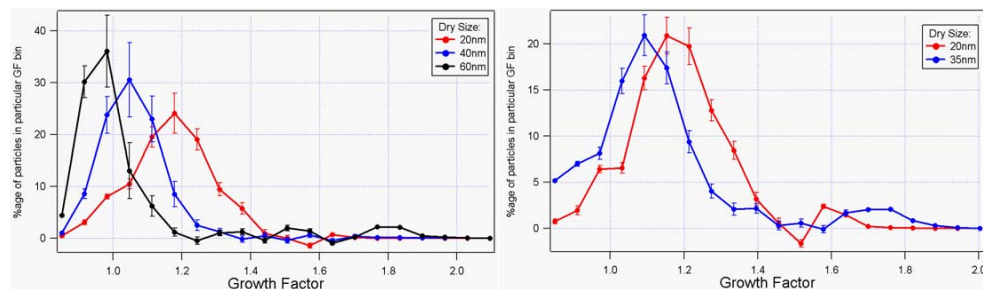


Fig. 7. Growth factor of particle formed in the **(a)** light and **(b)** dark reactions of molecular iodine and ozone. The growth factor is the ratio of the mobility sizes measured at 90% relative humidity and at <10%. It can be seen that those particles that have grown to larger dry sizes in both experiments exhibit lower growth factors. In the light experiment, where particles of 60 nm diameter were formed in sufficient numbers to be sampled, a significant proportion of these particles were shown to shrink on exposure to high humidity. This is consistent with those formed on exposure of CH_2I_2 to ozone. One possible explanation is the collapse of aspherical particles due to capillarity effects as exhibited by soot agglomerates.

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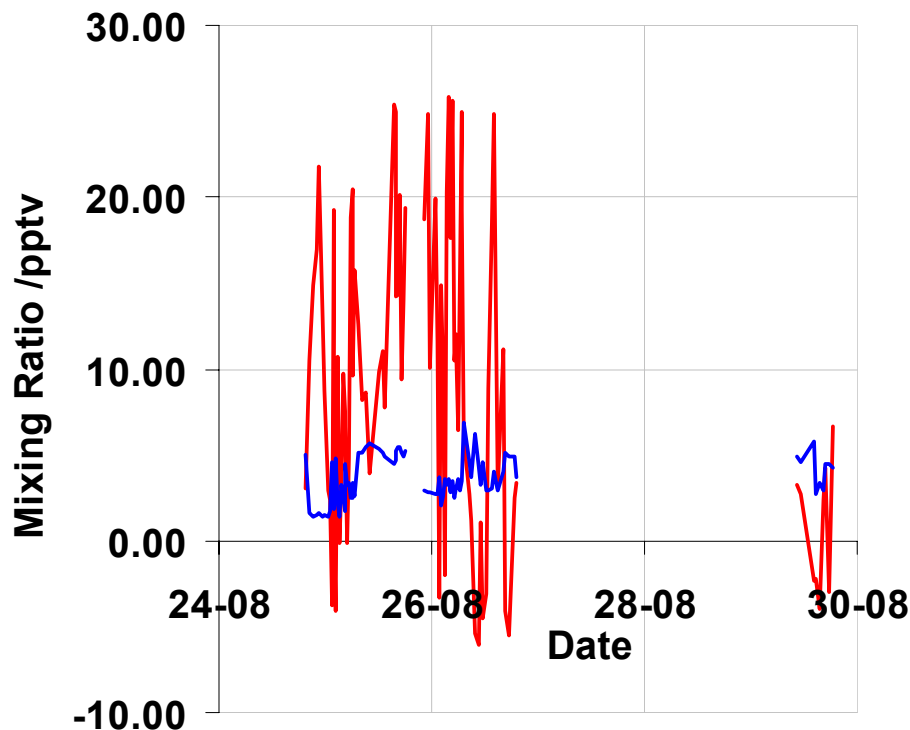


Fig. 8. DOAS measurements of I_2 from each of the three daytimes when spectra were recorded in the I_2 wavelength region (red trace). On 25 and 26 August 2002, the levels of I_2 were frequently above the detection limit (blue trace), reaching peak mixing ratios in excess of 25 parts per trillion (ppt).

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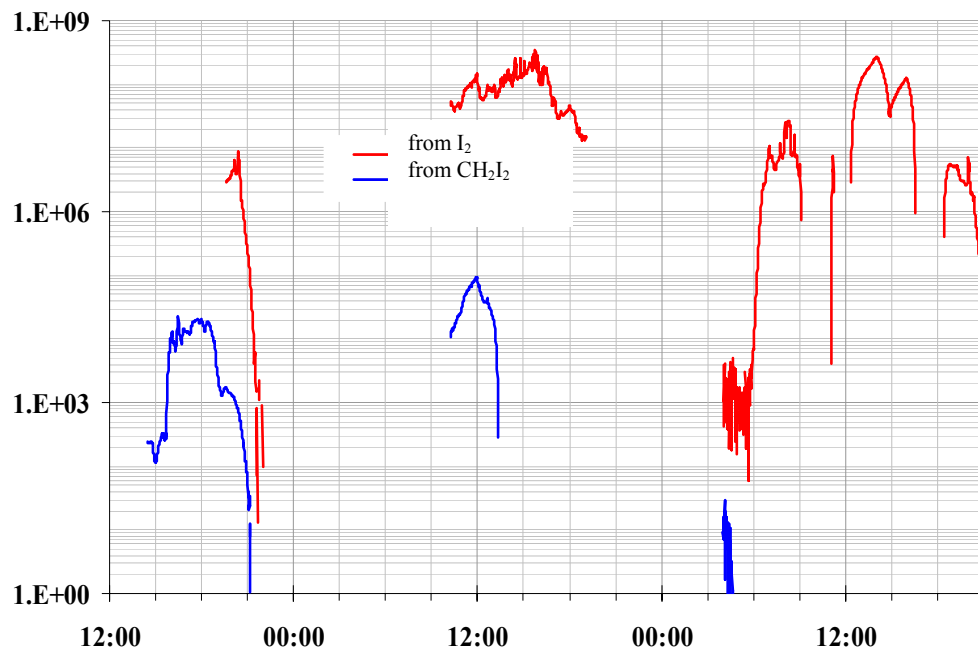


Fig. 9. Iodine atom flux from the photolysis of I_2 and CH_2I_2 at Mace Head on 25 and 26 August 2002 (note that there were no measurements of CH_2I_2 after dawn on 26 August). It can be seen that there was at least three orders of magnitude greater atomic iodine flux from the photolysis of the available molecular iodine than from the photolysis of CH_2I_2 ; on many occasions this difference was much greater.

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